International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : B05D 1/32, 5/12, B05C 17/06 | A1

(11) International Publication Number: WO 00/21689

(43) International Publication Date: 20 April 2000 (20.04.00)

(21) International Application Number: PCT/US99/23717

(22) International Filing Date: 8 October 1999 (08.10.99)

(30) Priority Data:
60/103,790 9 October 1998 (09.10.98) US

(71) Applicant *(for all designated States except US)*: THE TRUSTEES OF PRINCETON UNIVERSITY [US/US]; Fifth Floor, New South Building, Post Office Box 36, Princeton, NJ 08544-0036 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: CHOU, Stephen, Y. [US/US]; 7 Foulet Drive, Princeton, NJ 08540 (US). ZHUANG, Lei [CN/US]; C101, E-Quad, Dept of EE, Princeton University, Princeton, NJ 08544-0036 (US).

(74) Agent: MILLER, Raymond, A.; Reed Smith Shaw & McClay LLP, P.O. Box 488, Pittsburgh, PA 15230-0488 (US).

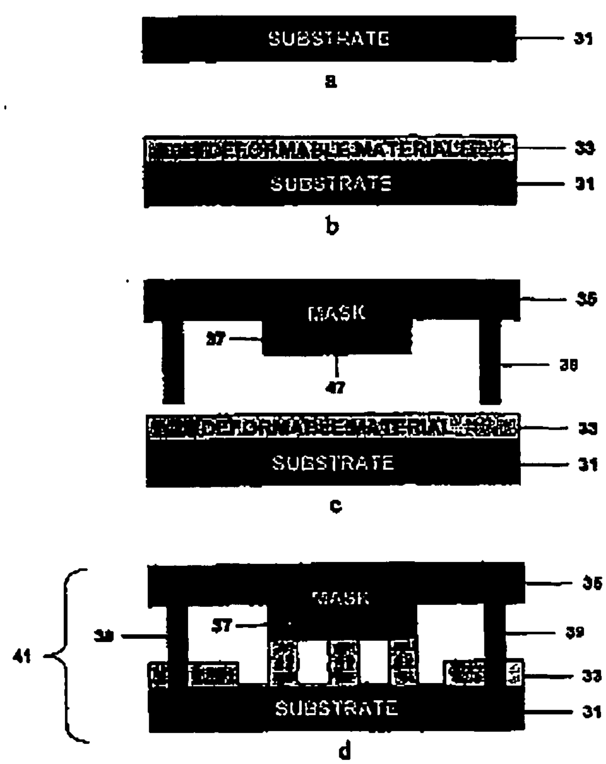
(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: MICROSCALE PATTERNING AND ARTICLES FORMED THEREBY

(57) Abstract

The present invention is directed to a lithographic method and apparatus for creating micrometer sub-micrometer patterns in a thin film coated on a substrate. The invention utilizes the self-formation of periodic, supramolecular pillar arrays (49) in a melt to form the patterns. The self-formation is induced by placing a plate or mask (35) a distance above the polymer film (33). The pillars bridge the plate and the mask, having a height equal to the plate-mask separation and preferably 2-7 times that of the film's initial thickness. If the surface of the mask has a protruding pattern, the pillar array is formed with the edge of the pillar array aligned to the boundary of the mask pattern.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

MICROSCALE PATTERNING AND ARTICLES FORMED THEREBY

GOVERNMENT INTEREST

This invention was made with Government support under Contract No. 341-6086 awarded by DARPA. The Government has certain rights in this invention.

CROSS REFERENCE TO RELATED APPLICATION

The benefit of U.S. Provisional Patent Application Serial No. 60/103,790 filed on October 9, 1998 is claimed.

FIELD OF THE INVENTION

The present invention relates generally to forming patterns on or in a surface material, assemblies used therefor, and articles formed thereby. More specifically, the present invention relates to microscale patterning and/or lithography. Microscale patterning and microscale lithography have a broad spectrum of applications, e.g. in the production of integrated circuits, microdevices, and the like. The patterns formed can be utilized to perform an array of functions, including electrical, magnetic, optical, chemical and/or biological functions.

BACKGROUND

One of the key processing methods in fabrication of semiconductors, integrated electrical circuits, integrated optical, magnetic, and mechanical circuits and microdevices is forming very small patterns.

Lithography is often used to create a pattern in a thin film carried on a substrate so that, in subsequent process steps, the pattern will be replicated in the substrate or in another material which is added onto the substrate. One purpose the thin film satisfies is protecting a part of the substrate so that in subsequent replication steps, the unprotected portion can be selectively etched or patterned. Thus, the thin film is often referred to as a resist.

A typical lithography process for the integrated circuits fabrication involves exposing a resist with a beam of energetic particles which are electrons, or photons, or ions, by either passing a flood beam through a mask or scanning a focused beam. The particle beam changes the chemical structure of the exposed area of the film, so that when immersed in a developer, either the exposed area or the unexposed area of the resist will be removed to recreate the pattern or obverse of the pattern, of the mask. A limitation on this type of lithography is that the resolution of the image being formed is limited by the wavelength of the particles, the particle scattering in the resist, the substrate, and the properties of the resist. Although pattern sizes greater than 200 nm can be achieved by photolithography, and pattern sizes in the range of 30 nm to 200 nm can be achieved utilizing electron beam lithography, these methods are resource intensity and suffer from low resolution.

U.S. Patent No. 5,772,905 describes a method and apparatus for performing ultra-fine line lithography wherein a layer of thin film is deposited upon a surface of a substrate and a mold having at least one protruding feature and a recess is pressed into the thin film.

An alternative strategy to those described above is to use a "naturally occurring" or "self-assembly" structure as a template for subsequent parallel fabrication. For example, U.S. Patent No. 4,407,695 and U.S. Patent No. 4,801,476 describe a spin coating technique to prepare close-packed monolayers or colloidal polystyrene spheres with diameters of typically 0.1-10 microns on solid substrates. The pattern is then replicated by

a variety of techniques, including evaporation through the interstices, ion milling of the spheres and/or the substrates, and related techniques. Highly ordered biologically membranes ("S-layers") have also been suggested as starting points for fabrication. Close packed bundles of cylindrical glass fibers, which could be repeatedly drawn and repacked to reduce the diameters and lattice constant have also been used. Block copolymer films have been suggested for use as lithography masks wherein micelles of the copolymer which form on the surface of a water bath are subsequently picked up on a substrate.

To date, the focus of "self-assembly" has been primarily on either phase separation of a polymer blend, of di-block copolymers, or of local modification of surface chemistry (*i.e.*, chemical lithography). In self-assembly by phase separation, the periodic structures are multidomain, and their orientation and locations are uncontrollable and random. A long-sought after goal in self-assembly is precise control of the orientation and location of a self-assembled polymer structure.

There is an ongoing need to produce progressively smaller pattern size. There also exist a need to develop low-cost technologies for mass-producing microscale and sub-micron (e.g. nanometer) structures. Microscale, indeed nanoscale and smaller, pattern technology will have an enormous impact in many areas of engineering and science. Both the future of semiconductor integrated circuits and the commercialization of many innovative electrical, optical, magnetic, and mechanical microdevices that are far superior to current devices will depend on such technology.

SUMMARY OF THE INVENTION

Technologically, self-assembly promises not only low-cost and high-throughput, but also other advantages in patterning microstructures, which may be unavailable in conventional lithography.

The present invention is generally directed to the formation of patterns in a material through deformation induced by a mask placed above a material, as well as assemblies used therefor, and products formed thereby. An important aspect of the present invention is novel method, referred to herein as "lithographically-induced self-assembly" (LISA). In this process a mask is used to induce and control self-assembly of a deformable surface, preferably a thin film into a pre-determined pattern. One advantage of the present invention is relatively accurate control of the lateral location and orientation of a self-assembled structure. Preferably, a substantially uniform, film is cast on a substrate. A mask, preferably with protruding patterns representing the pattern to be formed in or on the film, is placed above the film, but physically separated from the film by a gap. The mask, the film, and the substrate are manipulated, if necessary, to render the film deformable. For example in the case of a polymer, the polymer film may be heated to a temperature above the polymer's glass transition temperature and then cooled down to room temperature. During the heat-cool cycle, the initially flat film assembles into discrete periodic pillar arrays. The pillars, formed by rising against the gravitational force and surface tension, bridge the two plates to form periodic pillar arrays. The pillars generally have a height equal to the plate-mask separation. Moreover, if the surface of the mask has a protruding pattern, the pillar array is generally formed only under the protruding pattern with the edge of the array generally aligned to the boundary of the mask pattern. After the pillar formation, due to a constant polymer volume, there is little polymer left in the area between pillars. The shape and size of the mask pattern can be used to determine the pillar array's lattice structure. The location of each pillar can be controlled by the patterns on the mask. This process can be used repeatedly to demagnify the self-assembled pattern size. This demagnification permits a

self-assembled structure to have a size smaller than that of the mask pattern(s). If the demagnification is used repeatedly, a size much smaller than that by a single self-assembly process can be achieved. This would allow for progressively smaller pattern-mask-patterns to be formed. The basic LISA process can also be modified to form a non-pillared pattern that is substantially identical to the features of the mask.

One embodiment of the present invention is a patterning method or method of patterning which comprises depositing a material on a substrate. The material and substrate may be already formed, and the material and substrate may be the same or different. In this case the step of depositing a material would not be necessary, but rather a surface layer(s) would be selectively manipulated so that a pre-determined thickness of surface material is deformable. This thickness must be small enough that the mask can interact with the material through the separation distance to form a contact therebetween. As is described more fully herein, the thin film or surface layer(s) preferably has a thickness in the range of about 1 nm to about 2,000 nm, more preferably about 10 nm to about 1,000 nm, more preferably about 100 nm to about 500 nm and even more preferably about 50 nm to about 250 nm. If the deposited material is deformable at room temperature (e.g., a liquid polymer or polymer dispersion, the material may not need to be deformed). If a liquid polymer is used, it may be cured (e.g., photo curing) after either pillar formation, usually before removal of the mask. For a solid material, it may be necessary to render the material deformable, e.g. by heating to a temperature where the material may flow. Deforming by heat is a preferred route, but the material or surface layer(s) may also be deformed by other routes (e.g., chemical reactions). Heating may occur by any conventional means (e.g., laser, light sources, heat radiating or microwave induction), and the heat may be pulsed or continuous.

It is important that the mask be maintained above the material or film. A spacer (which may be integrally or non-integrally formed with the mask) is convenient to this end. However, an assembly may be used wherein the mask is maintained above said material without resorting to a spacer.

The substrate can be any number of compositions which are capable of supporting the film, but the present invention has particular applicability to substrates which are, themselves intended to be processed to have patterns formed thereon or therein. The substrate can have pre-existing relief patterns or be flat.

The mask can be of any suitable material as described herein. in many cases, the mask, will often be very similar in composition to the underlying substrate. Indeed, it is envisioned to use a suitably patterned substrate from a previous LISA process in a second or more LISA process or LISC process. The mask can have any suitable surface coating and the protrusion may be formed from a surfactant or other suitable protruding material (e.g., monolayers or self-assembled monolayers) with a different surface energy. The protruding pattern may be of varying heights on the same pattern resulting in like pillars. Of course, any combination of protrusion pattern protrusion coating or monolayer material pattern may be used to form the relief structure.

Another embodiment of the present invention is the relief structure formed by either or both the LISA and LISC process.

BRIEF DESCRIPTION OF THE DRAWINGS

The features, aspects, and advantages of the present invention will become better understood with regard to the following description, appended claims, and accompanying drawings wherein:

Fig. 1 schematically illustrates lithographically-induced self-assembly (LISA): (a) a flat substrate, (b) a thin layer of deformable material deposited thereon, (c) a mask with a protruding pattern a distance above the deformable material; and (d) self-assembly into a periodic supramolecular pillar array after a heat-and-cool cycle;

Fig. 2 is an (a) optical and (b) AFM images of periodic pillars formed using a mask of a plain flat surface. The pillars have a closely-packed hexagonal lattice and are multi-domain, covering the entire wafer with a single-domain size of about 50 μm;

Fig. 3 is an optical micrograph of (a) a protruding triangle pattern on the mask and (b) pillar array formed under the triangle pattern using LISA, and (c) AFM of the pillar array;

Fig. 4 is an optical and AFM images of the LISA pillar arrays formed under protruding square patterns of a side of (a) 10 μm, (b) 14 μm, and (c) 14 μm. The separation between the mask and the substrate (a) 430 nm, (b) 280 nm, and (c) 360 nm, respectively;

Fig. 5 is (a) optical micrograph of a protruding line pattern spelling "PRINCETON" on the mask and (b) AFM image of pillars formed under the mask pattern;